# Role of water on formation and structural features of Maya blue

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**Abstract.** The Maya blue (MB) is an artificial pigment created between 500-800 A.D. and used in murals, pottery and sculptures by Mayas and other people in Mesoamerica. MB is resistant to age, acid, weathering, biodegradation and even modern chemical solvents, but the chemical reasons behind the resistance to chemical aggressions are still under debate. Water plays a fundamental role in the interactions between indigo and clay. The dynamics of the clay's zeolitic and structural water molecules during the formation of MB, usually stabilized by moderate heating, has been monitored by means of neutron inelastic scattering. Neutron incoherent scattering in these samples is only due to the hydrogen atoms, so the signal is very sensitive to the amount of released water, providing detailed information on the dehydration process. A simultaneous analysis of the coherent elastic scattering and the incoherent scattering allows observing and quantifying how the structure of the clay is affected by dehydration. Here we show that a quite resistant pigment can be obtained at room temperature simply by dehydrating a palygorskite-indigo mixture employing only vacuum, without any thermal treatment.

## 1. Introduction

Maya blue [1] is an artificial pigment fabricated by the Maya in the first millennium A.D. The pigment was used in Prehispanic times from the southern Maya region to most Mesoamerican cultures. In ancient times, the fabrication and distribution of this pigment probably required a sophisticated technical and commercial infrastructure. Maya blue is made from indigotin mixed with palygorskite. Palygorskite is a fibrous clay featuring channels in its structure, which are filled by zeolitic $H_2O$. Palygorskite has a great absorbing power, and can also be used as a carrier for organic molecules, as well as for drugs. MB can be easily fabricated by crushing a few percent of indigotin with palygorskite powder. After this, a mild heating (~200°C during a few hours) is necessary to make this light blue

pigment surprisingly resistant to degradation in adverse environmental conditions, as it is unaffected by the attack of acids, alkalis, oxidants, reducing agents and organic solvents [2]. Scientists still do not fully agree in the mechanism of this organo-clay interaction [3]. It has been proposed that a partial or perhaps total evacuation of the zeolitic $H_2O$ is essential to allow the indigo to either penetrate in the tunnels or to sit and block the entrance of the tunnels [4]. In this work we apply neutron scattering to monitor the dehydration of palygorskite during the formation of MB. In particular, we study here whether the dehydration of the clay, obtained only by vacuum pumping, is a sufficient condition for stabilizing MB, or if a subsequent heating is required.

## 2. Experimental details

Indigo was purchased from Sigma Aldrich. Palygorskite (theoretical molecular formula $Si_8(Mg_2Al_2)O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ ) is a natural clay coming from Ticul, in Yucatán (Mexico). This palygorskite has been thoroughly studied [5]. The mixture of palygorskite equilibrated at ambient conditions and indigo was finely crushed in a mortar. For the present study, different samples of 0.7 g each have been prepared from the starting mixture having a content of indigo of 3% in weight. In situ inelastic neutron scattering measurements were performed on the Time-of-Flight spectrometer IN6 at the Institut Laue-Langevin (Grenoble). They were performed using an incident wavelength of 5.1 Å and the angular range covered was $10° \leq 2\theta \leq 115°$. Two different sets of measurements were done: One of the samples was measured only at room temperature, but applying a continuous pumping (vacuum $\sim 10^{-3}$ Torr) on it and acquiring data as a function of time. The second sample was subjected to the thermal treatment exemplified by the temperature ramp ($300 \leq T(K) \leq 520$) shown in Fig. 2. We applied to the data the standard corrections and calibration (subtraction of the empty cell signal and detector efficiency calibration). In all cases the transmission was higher than 90%, so no multiple scattering corrections has been applied.

**Table 1.** Coherent and incoherent cross sections for a unit formula of palygorskite ($Si_8(Mg_2Al_2)O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$) and indigo ($C_{16}H_{10}N_2O_2$). The numbers between parentheses indicate the number of atoms of each element in the sample.

| Palygorskite | $\sigma_{coh}$ (barn) | $\sigma_{inc}$ (barn) |
|---|---|---|
| Si (8) | 17.30 | 0.03 |
| Mg (2) | 7.26 | 0.16 |
| Al (2) | 2.99 | 0.16 |
| O (30) | 126.96 | 0.02 |
| H (18) | 31.62 | 1444.68 |
| **Total** | **186.13** | **1445.05** |
| Indigo | $\sigma_{coh}$ (barn) | $\sigma_{inc}$ (barn) |
| C (16) | 88.82 | 0.02 |
| N (2) | 22.04 | 1.00 |
| O (2) | 8.46 | 0 |
| H (10) | 17.57 | 802.60 |
| **Total** | **136.89** | **803.62** |

## 3. Results and discussion

In order to quantify the incoherent and coherent signals, related to the content of water and the atomic structure of the sample, respectively, we have evaluated the coherent and incoherent cross sections of the elements present in the samples (Table 1). The incoherent signal is mainly due to the atoms of hydrogen in the zeolitic and structural water molecules, together with the contribution of the structural OH groups in palygorskite and the H atoms in indigo. In addition, some hydration water present on the surface of the clay can contribute to it. This hydration water is rapidly lost when the vacuum or the thermal treatments are applied (Figures 1 and 2). The incoherent signal coming from the structural OH groups and the indigo is subtracted based on the chemical formulas of the constituents, so the remaining signal contains two equal contributions due to the four structural water molecules and the four zeolitic ones. This procedure allows following the formation of a pigment having the same characteristics of the ancient MB by monitoring the amount of structural and zeolitic waters in the samples under the hypothesis that the zeolitic water evacuates completely from the sample before the structural water starts to escape. In order to do this, we need to separate the incoherent and coherent contributions in the measured signal, so we integrated in energy the measured dynamical structure factor, $S(Q,\omega)$, and then we separated the elastic scattering $S(Q)_{coh}$ (assumed to correspond to the area below the Bragg peaks) from the incoherent flat signal using the XOP program [6].

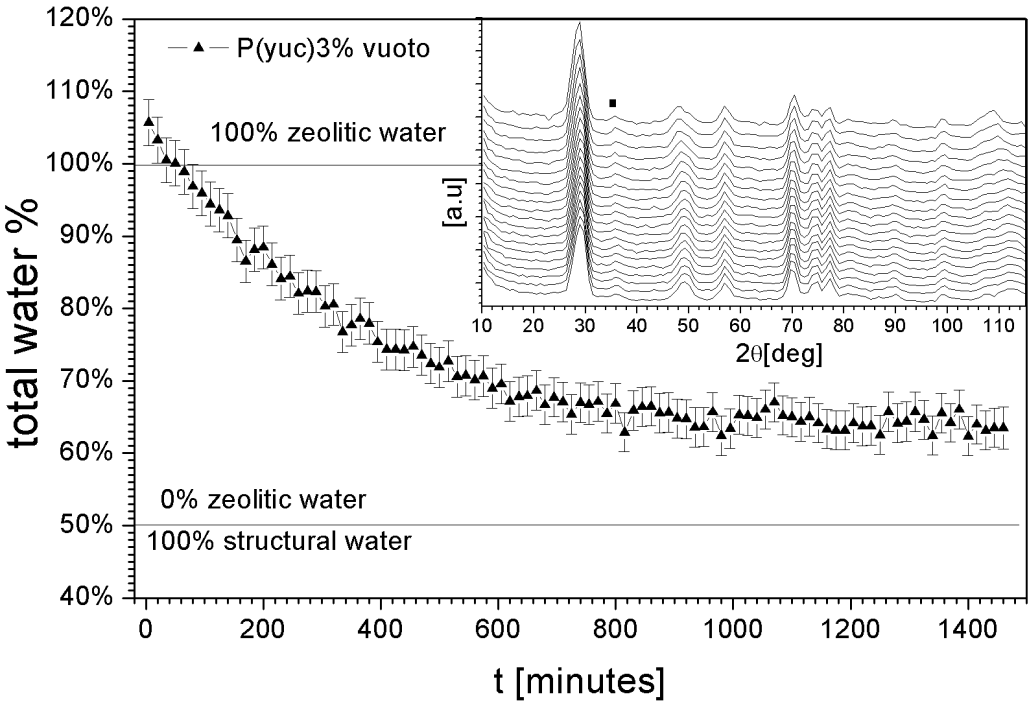


**Figure 1.** Percentage of water as a function of time in a mixture of palygorskite and 3% of indigo, when a continuous pumping is applied. A limiting value of 30% of zeolitic water remaining inside the palygorskite is reached after 800 minutes. The inset shows the elastic coherent signal measured at different times (time increasing from top to bottom). The peak marked with a square in the top curve corresponds to pure indigo that has not gone into the clay. The other peaks correspond to the structure of the palygorskite + indigo.

Figure 1 shows the evolution as a function of the time of the percentage of zeolitic and structural water, calculated as described in the previous paragraph. A continuous pumping is applied at time zero and the change of slope of the curve is related to the rate of water loss. It can be observed the

contribution of the different types of water: a first quick loss corresponds to the hygroscopic water adsorbed to the clay and then the sample loses zeolitic $H_2O$ progressively. In this case, all changes in water content are only due to the effect of vacuum, as no heating was applied. It is evident how the vacuum causes a partial loss of the total amount of water in the sample.

The hygroscopic $H_2O$ is completely lost, plus an important part of the zeolitic $H_2O$. However the 30% of the total zeolitic water remains in the sample even after 8 hours of pumping. In the inset of figure 1 the peaks corresponding to the crystallographic structure of the mixture of palygorskite and indigo are reported. The crystallographic structure does not present relevant structural changes due to the vacuum, but we can observe a slow decrease of the intensity of the peak of un-reacted indigo (indicated with a square in the inset).

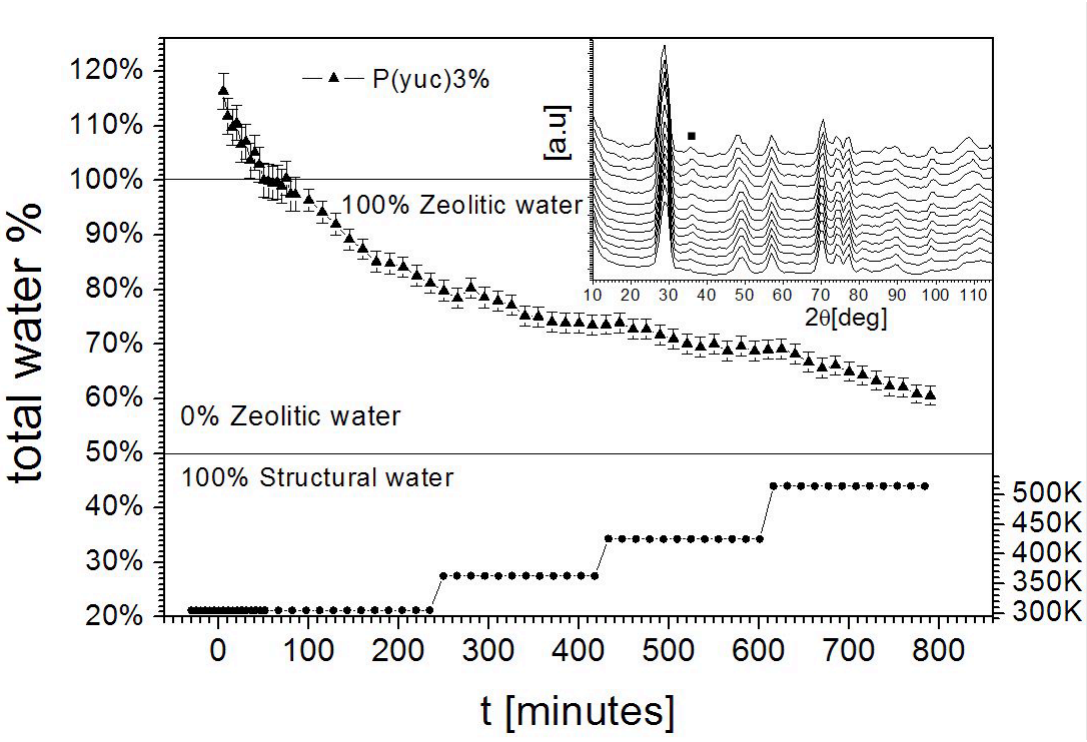


**Figure 2.** Change in the percentage of water as a function of time in a mixture of palygorskite and 3% of indigo when the thermal treatment indicated by the dots in the bottom of the picture is applied. As in the previous figure, the inset shows the elastic coherent signal measured at different times (time increasing from top to bottom).

A similar set of measurements was done using a second sample coming from the same bunch, but in this case applying a thermal treatment. The temperature ramp employed and the changes in the water content observed are reported in figure 2. The maximum temperature attained (520 K) corresponds to the temperature needed to produce a final pigment with the same stability as the original MB. Comparing with figure 1, we observe that the value of 30% of zeolitic water remaining in the sample is reached after only 650 minutes and that contrary to the previous case, the loss of water continues below this limit. Additionally we observe that the peak of un-reacted indigo disappears completely. We conclude that the thermal treatment anticipates the dehydration of the indigo-palygorskite mixture, but that the initial mechanism of water lost is equivalent down to 30% of zeolitic $H_2O$ remaining in the sample.

In order to test the stability of the complexes formed by both methods, the final samples obtained from both experiments (with and without heating) were immersed in concentrated $HNO_3$ for at least 5 minutes. The high oxidant power of $HNO_3$ destroys the indigo molecules, a process that is accompanied by a complete lost of the blue colour. If indigo is just crushed with palygorskite, and the result is immersed in $HNO_3$, a complete decolouration is also observed because the indigo is not yet stabilized. However when the palygorskite stabilizes the indigo, e.g. after the heating process, the resulting complex becomes resistant and does not decolour in acid. After immersion in acid, the sample obtained by applying only vacuum shows a blue colour indicating that the MB pigment has been formed. However, a light decolouration is observed, indicating that not all the indigo was transformed into MB. On the contrary, the second sample (where heating was applied) did not show any decolouration, indicating a complete transformation of the indigo in MB. The resulting MB pigments are quite dark compared with the original Maya blue, which is much more turquoise, but this is surely due to the high content of indigo used in our samples (3%), while the quantity used by the Maya was probably around 1%. In figure 3 we compare the two pigments obtained in situ during the experiment. A higher content of indigo was employed to enhance the observed effects and facilitate the analysis, but the results with indigo contents less than approx 5% are certainly applicable to the ancient Maya blue with less indigo.

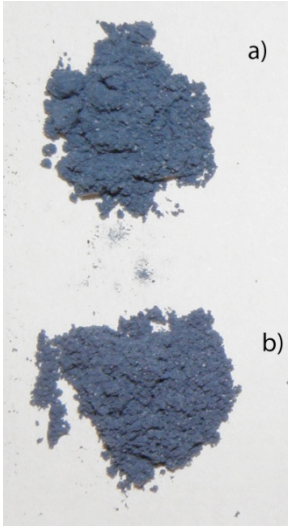


**Figure 3.** a) MB pigment obtained using only vacuum; b) MB pigment obtained using a thermal treatment. Both pigments are darker than the original MB due to the larger content of indigo employed in their preparation (3% instead of ≈ 1% used by the Mayas).

## 4. Conclusions

We have studied the lost of water during the formation of the final MB-type pigment by means of inelastic neutron scattering. As in our samples the incoherent scattering comes only from the hydrogen atoms, the measured signal is very sensitive to the amount of released water, providing quantitative information on the dehydration process. The simultaneous analysis of the incoherent and the coherent elastic scattering gave us a unique possibility to observe in parallel the dehydration process and the changes on the structure of the pigment. We show that the treatments applied are not strong enough to evacuate structural water and we quantify the amount of zeolitic water released during the MB formation. A quite resistant pigment is obtained from the zeolitic dehydration process of the palygorskite-indigo mixture only by means of vacuum, without any thermal treatment. This fact indicates that indigo bonds to palygorskite during the dehydration process, forming a stable pigment. This process is accelerated when heating is applied, but heating is not required to stabilize the pigment.

## Acknowledgments

We acknowledge the ILL for the allocated beamtime and for financial support (ILL stage). Financial support from the Spanish CICYT (project CGL2006-09843) is also gratefully acknowledged.

## References

[1] Reyes-Valerio C 1993 *De Bonampak al Templo Mayor. El azul maya en Mesoamerica: Colección America Nuestra* vol 40 (Mexico DF: Siglo XXI editores) p 157
[2] Van Olphen H 1966 *Science* **154** 645
[3] Sánchez del Río M, Doménech A, Doménech-Carbó M T, Vázquez de Agredos Pascual M L, Suárez M and García-Romero E 2011 *The Maya Blue Pigment* vol 3 Collection: Developments in Clay Science Chapter 18, ed A. Singer and E. Galan (Amsterdam, Elsevier)
[4] Giustetto R, Levy D, Chiari G 2006 *Eur. J. Mineralog.* **18** 629
[5] Sánchez del Río M, Suárez M, and García-Romero E 2009 *Archaeometry* **51** 214
[6] Sanchez del Rio M and Dejus R J 2001 XOP 2.1 *A new version of the x-ray optics software toolkit* American Institute of Physics Conference Proceedings **705** 784